

**STUDIES ON
AROMATIC—ALIPHATIC COPOLYESTERS**

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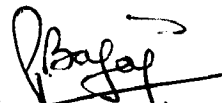
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**IN MEMORY
OF
MY BELOVED FATHER**

CERTIFICATE

This is to certify that the thesis entitled "STUDIES ON AROMATIC-ALIPHATIC COPOLYESTERS" being submitted by Mr. Dinesh Narain Khanna to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Textile Technology, is a record of bonafide research work carried out by him. Mr. Dinesh has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results given in this thesis have not been submitted in part or in full, to any other University or Institute for the award of any degree or diploma.


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ABSTRACT

The present thesis deals with the synthesis, characterization, and structure-properties relationship of aromatic-aliphatic copolyesters with some new combinations of bisphenols and glycols. Various polycondensation processes such as interfacial, low and high-temperature solution condensation, melt and melt-solid condensation have been adopted for synthesizing aromatic-aliphatic copolyesters. 2,2-bis(4-hydroxyphenyl) propane, 4,4'-dihydroxybiphenyl, 4,4'-dihydroxydiphenyl sulphone, resorcinol, hydroquinone, and phenolphthalein were selected as aromatic diols, and ethylene glycol and polyethylene glycol (PEG,²⁰⁰ PEG¹⁰⁰⁰) as aliphatic diols.

The polymers prepared were characterized for their solubility, softening temperature, and solution viscosity. The structure elucidation of polymers was carried out by infrared (IR), nuclear magnetic resonance (NMR), and X-ray diffraction methods. End group analysis technique was adopted for molecular weight (\bar{M}_n) determination. It was observed that copolymers have low molecular weight than their respective homopolymers.

Solubility of polymers was tested in various solvents. It is interesting to note that the polymer, P_I^{*}, synthesized by using ethylene glycol (EG) and terephthaloyl chloride (TCI) by interfacial polycondensation was found to be

insoluble in most of the solvents in contrast to polyester synthesized by employing EG and TCl by low temperature (LT) and high temperature (HT) solution methods.

Unlike PET (synthesized by melt condensation), a characteristic band at 1818 cm^{-1} was observed in P_{I}^* sample, which has been assigned to one of the anhydride carbonyl bands. Similar IR absorption band has also been observed in copolyesters (having high content of EG or PEG in the feed) prepared by interfacial polycondensation. PET prepared by high temperature solution method also showed a weak anhydride carbonyl band at 1818 cm^{-1} . Moreover, X-ray diffraction pattern and softening temperature of P_{I}^* is also different from PET synthesized by other methods. On the basis of insolubility, IR spectra and X-ray diffractogram, it is assumed that P_{I}^* obtained by interfacial polycondensation method is chemically different from PET, presumably having major sequences of poly(terephthalic anhydride).

Melt and melt-solid condensation processes have also been used for the synthesis of aromatic-aliphatic copolyesters with limited mole ratios (upto 10.0 mole%) of various bisphenols.

Thermal behaviour of copolyesters was studied in detail by thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermal decomposition of copolyesters was expressed in terms of initial decomposition

temperature (IDT), integral procedural decomposition temperature (IPDT), and activation energy (E^*). Thermal stability in N_2 was higher than in air. Thermal stability of copolyesters was low as compared to homopolyesters. Various parameters such as, T_g , T_m , T_c , ΔH_f , ΔH_c , degree of crystallinity, and crystallization were evaluated. Effect of cooling rate (40, 20 and $5^\circ C \text{ min}^{-1}$), room temperature cooling and quenching in liquid nitrogen, on crystallization of copolyesters has also been studied. Among the copolyesters, resorcinol and Bisphenol-A copolyesters had better crystallizability than hydroquinone and Bisphenol-S copolyesters. In aromatic-aliphatic copolyesters, resorcinol perhaps serves as a nucleating agent which increases the overall rate of crystallization, whereas hydroquinone and Bisphenol-S hinder the crystallization, and thereby affect the final properties of the corresponding copolyesters.

In copolyesters (with 10 mole % of various bisphenols), the X-ray crystallinity follows a trend similar to that of DSC. Crystal lattice did not change by the incorporation of limited amount of bisphenols in aromatic-aliphatic copolyesters, whereas wholly aromatic polyesters showed a difference in the lattice structure.

Copolyesters synthesized by incorporating 10 mole % of various bisphenols were spun into fibres by melt spinning process. As-spun fibres were drawn to 4-5 draw ratio and heat-set at 135°C for 30 min in air oven at constant length. Physico-mechanical and dynamic-mechanical properties of these fibres were measured using Instron, Rheovibron, and Sonic-Modulus tester. The copolyester fibres showed a drop in mechanical properties as compared to PET.

The dyeing was carried out using C.I. Disperse Red-17 at 80, 100, and 120°C using different intervals of time (15 to 180 min). The dyeing behaviour of the fibres was expressed in terms of diffusion coefficient, activation energy of dye diffusion, and dye-uptake. Copolyester fibres showed better dye-uptake and moisture sorption as compared to PET. Among copolyesters, Bisphenol-S and hydroquinone copolyesters showed better dye-uptake and moisture sorption than those of Bisphenol A and resorcinol copolyesters. The difference in dye-uptake is due to the difference in the amorphous content of the fibres. The copolyesters were also less flammable than PET. On the whole, the incorporation of bisphenols affects the structure, and thereby the properties of copolyesters.

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